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National Food Safety Standard-New Red

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FAIRS Subject Report

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Report Highlights:
On May 5, 2010, China notified the WTO of National Food Safety Standard: Food Additives – New Red as SPS/N/CHN/278. This measure applies to the production, circulation, supervision and management of the food additive new red. It specifies the scope, requirements and testing methods. The date for submission of final comments to China is May 20, 2010. The proposed date of entry is May 30, 2010. Contact information on where to send comments is inside the report. This report is an INFORMAL translation of this document.

Executive Summary:
On May 5, 2010, China notified the WTO of National Food Safety Standard: Food Additives – New Red as SPS/N/CHN/278. This measure applies to the production, circulation, supervision and management of the food additive new red. It specifies the scope, requirements and testing methods. The date for submission of final comments to China is May 20, 2010. The proposed date of entry is May 30, 2010.

Comments can be sent to the China WTO SPS Enquiry Point at: SPS@aqsiq.gov.cn.

This report contains an UNOFFICIAL translation of National Standard on Determination of New Red in Foods.

General Information:
BEGIN TRANSLATION

GB National Food Safety Standard

GB 6227.1-XXX

Food Additive - New Red

National Food Safety Standard

(Draft for Comment)

Issued on xx-xx-xxxx
Implemented on xx-xx-xxxx
Issued by the Ministry of Health
of the People's Republic of China

Foreword

This Standard supersedes GB 14888.1-1994 Food Additive - New Red.

Compared with GB 14888.1-1994, this Standard has the following main changes:

-- modifying appearance from red powder into red brown powder or granule;

-- modifying content requirement from ≥ 80 % to ≥ 85 %;

-- modifying identification method;

-- modifying permissible difference for parallel determination by spectrophotometric colorimetric method from 2 % to 1.0 %;

-- adding control requirements and test methods for chloride and sulfate and combining control requirement for loss on dry to reach ≤ 15.0 %;

-- cancelling control requirement for isopropyl ether extract;

-- adding control requirement and test method for sum of unreacted intermediates;

-- adding control requirement and test methods for unsulfonated aromatic primary amine (based on aniline);

-- modifying test method of arsenic from chemical half-limit test method into atomic absorption method; and

-- modifying requirement for heavy metals (based on lead) into control requirement for lead and test methods into atomic absorption method.

Annex A, Annex B, Annex C and Annex D of this Standard are normative.

This Standard supersedes the following previous edition:

-- GB 14888.1-1994

National Food Safety Standard

Food Additive – New Red

1 Scope

This Standard is applicable to quality control of new red products made by salting out and refining after coupling diazotized aminobenzene sulfonic acid with 5-acetamino-4-naphthol-2,7-sodium disulfonate.

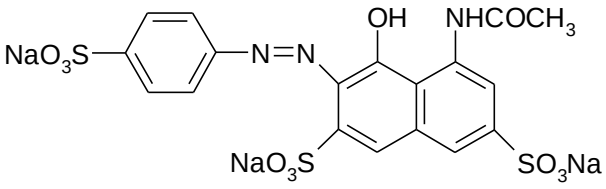
2 Normative references

Documents referenced in this Standard are indispensable for the application of this Standard. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

3 Chemical name, structural formula, molecular formula and relative molecular mass

Chemical name: disodium salt of 7-[(4-sulfophenyl)azo]-1-acetamino-8-naphthol-3, 6-disulfonate

Structural formula:



Molecular formula: C18H12O11N3Na3S3

Relative molecular mass: 611,47 (based on 2007 International Relative Atomic Mass)

4 Technical requirements

Technical requirements of new red shall be in accordance with Table 1.

Table 1 Technical requirements of new red

Items	Requirement	Test method
Appearance	Red brown powder or granule	Visual inspection under natural light
New red, *w*/%	≥85.0	A.3 in Annex A
Loss on drying, chloride and sulfate (based on sodium salt), *w*/%	≤15.0	A.4 in Annex A
Water insoluble matter, *w*/%	≤0.20	A.5 in Annex A
Subsidiary colors, *w*/%	≤2.0	A.6 in Annex A
Sum of unreacted intermediates, *w*/%	≤0.50	A.7 in Annex A
Unsulfonated aromatic primary amine (based on aniline), *w*/%	≤0.01	A.8 in Annex A
Arsenic/(mg/kg)	≤1.0	A.9 in Annex A
Lead/(mg/kg)	≤10.0	A.10 in Annex A

Annex A

(Normative)

Test Method

A.1 General requirements

Reagents and water used in this Standard, unless otherwise stated, are analytically pure reagents and grade III water specified in GB 6682-2008. Standard solution, impurity standard solution, preparations and products required in the tests of this Standard, unless otherwise stated, shall be prepared and calibrated according to requirements of GB/T 601, GB/T 602 and GB/T 603. Test results shall be judged in accordance with 4.3.3 round-off comparison method in GB/T 8170-2008.

A.2 Identification

A.2.1 Reagents and solutions

a) Sulfuric acid;

b) Ammonium acetate solution: 1.5 g/L.

A.2.2 Apparatus

a) Spectrophotometer;

b) Cuvette: 10 mm.

A.2.3 Identification method

Weigh about 0.1 g of the sample (accurate to 0.001 g), dissolve in 100 mL of water, and the resulting solution is red clear solution.

Weigh about 0.2 g of the sample (accurate to 0.001 g), dissolve in 20 mL of sulfuric acid, the resulting solution develops dark purplish red, add 2 - 3 drops of this solution to 5 mL of water, and shake, the resulting solution develops red.

Weigh about 0.1 g of the sample (accurate to 0.001 g), dissolve in 100 mL of ammonium acetate solution, and add ammonium acetate solution to 1 mL of the resulting solution to make 100 mL. The maximum absorption wavelength of the resulting solution is 525 nm±2 nm.

A.3 Determination of new red

A.3.1 Titanium trichloride titration method (arbitrary method)

A.3.1.1 Method summary

In acid medium, azo group in new red is reduced and decomposed into amino compound by titanium trichloride, and content of amino compound is calculated based on consumption of titanium trichloride standard titration solution.

A.3.1.2 Reagents and materials

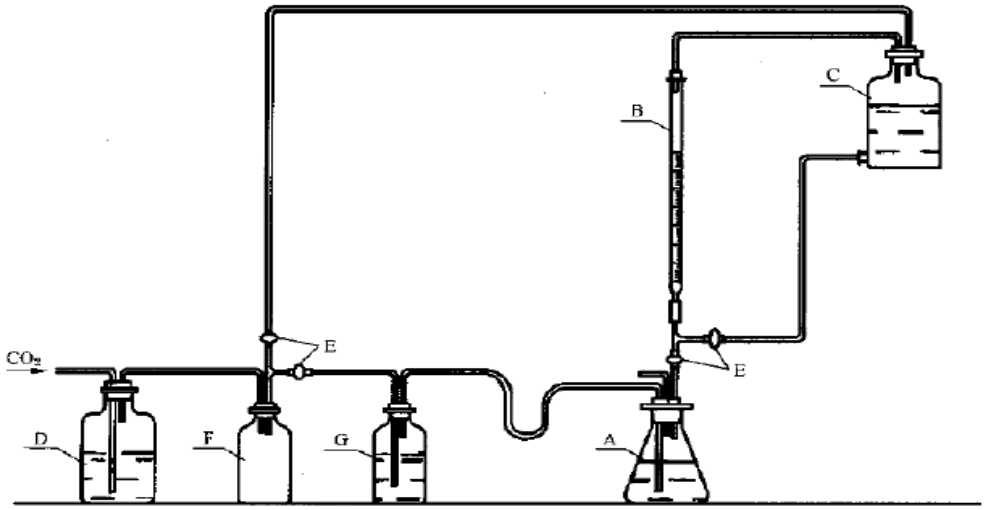
a) Trisodium citrate;

b) Titanium trichloride standard titration solution: c(TiCl3)=0.1 mol/L (freshly prepared; see Annex B for preparation method);

c) Carbon dioxide in steel cylinder.

A.3.1.3 Apparatus

See Fig. A.1.



A--conical flask (500 mL);

B--brown buret (50 mL);

C--glass bottle with mouth, wrapped by black paper (2000 mL);

D--container with mixture of equal volumes of 100 g/L ammonium carbonate solution and 100 g/L ferrous sulfate solution (5000 mL);

E--piston;

F--empty bottle;

G--gas washing bottle filled with water

Fig. A.1 Apparatus for titanium trichloride titration method

A.3.1.4 Determination procedures

Weigh about 0.5 g of the sample (accurate to 0.0001 g), placed to a 500 mL conical flask, add 15 g of trisodium citrate and 200 mL of freshly boiled water, shake for dissolving, install apparatus according to Fig.A.1, introduce carbon dioxide under liquid level while heating to boil, and titrate with titanium trichloride standard titration solution until the inherent color of mixture

disappears at the end point.

A.3.1.5 Result calculation

New red is calculated according to formula (A.1) based on mass fraction w1 and its value is expressed in %:

$$w_1 = \frac{c(V/1000)(M/4)}{m_1} \times 100 \quad \text{.....(A.1)}$$

where:

c--accurate value of concentration of titanium trichloride standard titration solution, expressed in g/mol;

V--accurate value of volume of titanium trichloride standard titration solution for titrating the sample, expressed in mL;

M--value of molar mass of new red, g/mol [M(C18H12O11N3Na3S3)=611.47];

m1--mass value of the sample, expressed in g.

Calculation result is rounded to 0.1.

A.3.1.6 Permissible difference

Absolute difference between two determination results is not more than 1.0 % (mass fraction) and arithmetic mean of the results is taken as determination result.

A.3.2 Spectrophotometric colorimetric method

A.3.2.1 Method summary

Dissolve the sample and new red standard substance with known content in water respectively, measure absorbance respectively at the maximum absorption wavelength, and then calculate the content

A.3.2.2 Reagents and solutions

a) Ammonium acetate solution: 1.5 g/L;

b) New red standard substance: ≥85.0 % (mass fraction, content is determined according to A.3.1 in this Standard).

A.3.2.3 Apparatus

a) Spectrophotometer;

b) Cuvette: 10 mm.

A.3.2.4 Preparation of new red standard sample solution

Weigh about 0.25 g of new red standard sample (accurate to 0.0001 g), dissolve in a proper amount of ammonium acetate solution, transfer to a 1000 mL volumetric flask, add ammonium acetate solution and dilute to volume and shake up, pipette 10 mL of the resulting solution to a 500 mL volumetric flask, add ammonium acetate solution and dilute to volume and shake up for use.

A.3.2.5 Preparation of new red sample solution

Weighing and operating methods are the same as A.3.2.4 Preparation of new red standard sample solution in this Standard.

A.3.2.6 Determination procedures

Place new red standard sample solution and new red sample solution in 10 mm cuvettes respectively, determine respective absorbance at the maximum absorption wavelength by spectrophotometer, and take ammonium acetate solution as reference solution.

A.3.2.7 Result calculation

New red is calculated according to formula (A.2) based on mass fraction w1 and its value is expressed in %:

$$w_1 = \frac{Am_0}{A_0 m} \times w_0 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (A.2)$$

where:

A--absorbance value of new red sample solution;

m0--mass value of new red standard substance, expressed in g;

A0--absorbance value of new red standard sample solution;

m--mass value of sample, expressed in g;

w0--value of new red standard sample, expressed in % (mass fraction).

Calculation result is rounded to 0.1.

A.3.2.8 Permissible difference

Absolute difference between two determination results is not more than 1.0 % (mass fraction) and arithmetic mean of the results is taken as determination result.

A.4 Determination of total loss on drying, chloride (based on NaCl) and sulfate (based on Na2S04)

A.4.1 Determination of loss on drying

A.4.1.1 Determination procedures

Weigh about 2 g of the sample (accurate to 0.001 g), place in a weighing bottle with constant weight, and bake in a 135 ℃ constant temperature oven to constant weight.

A.4.1.2 Result calculation

Loss on drying is calculated according to formula (A.3) based on mass fraction w2 and its value is expressed in %:

$$w_2 = \frac{m_2 - m_3}{m_2} \times 100 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (A.3)$$

where:

m2--value of sample before drying, expressed in g;

m3--value of sample dried to constant weight, expressed in g.

Calculation result is rounded to 0.1.

A.4.1.3 Permissible difference

Absolute difference between two determination results is not more than 0.2 % (mass fraction) and arithmetic mean of the results is taken as determination result.

A.4.2 Determination of chloride (based on NaCl)

A.4.2.1 Reagents and solution

a) Nitrobenzene;

b) Activated carbon: type 767 injection powder;

c) Nitric acid solution: 1+1;

d) Silver nitrate solution: c(AgNO3)=0.1 mol/L;

e) Ammonium ferric sulfate solution

Preparation method: weigh about 14 g of ammonium ferric sulfate, dissolve in 100 mL of water, filter, add 10 mL of nitric acid and store in a brown bottle;

f) Ammonium thiocyanate standard titration solution: c(NH4CNS)=0.1 mol/L.

A.4.2.2 Preparation of sample solution

Weigh about 2 g of the sample (accurate to 0.001 g), dissolve in 150 mL of water, add about 15 g of activated carbon, boil mildly for 2 - 3 min, add 1 mL of nitric acid solution, constantly shake up, and stand for 30 min (while constantly shaking). Filter by dry filter paper, add 5 g of activated carbon again if the filtrate is colored, stand for 1 h while shaking constantly, and filter by dry filter paper again (if filtrate still has color, replace activated carbon, and repeat the operation until the filtrate is colorless), wash activated carbon three times with 10 mL of water each time, combine filtrate and transfer to a 200 mL volumetric flask, add water to volume and shake up for determination of contents of chloride and sulfate.

A.4.2.3 Determination procedures

Transfer 50 mL of sample solution to a 500 mL conical flask, add 2 mL of nitric acid solution, 10 mL of silver nitrate solution (add more when chloride content is greater) and 5 mL of nitrobenzene, shake vigorously until silver chloride condenses, add 1 mL of ammonium ferric sulfate solution, and titrate excessive silver nitrate with ammonium thiocyanate standard titration solution to end point and keep for 1 min, and perform a blank test in the same way.

A.4.2.4 Result calculation

Chloride (based on NaCl) is calculated according to formula (A.4) based on mass fraction w3 and its value is expressed in %:

$$w_3 = \frac{c_1[(V_1 - V_0)/1000]M_1}{m_4(50/200)} \times 100 \quad \text{.....(A.4)}$$

where:

c1--accurate value of concentration of ammonium thiocyanate standard titration solution, expressed in g/mol;

V 1 --accurate value of volume of ammonium thiocyanate standard titration solution consumed for titrating blank solution, expressed in mL;

V0--accurate value of volume of ammonium thiocyanate standard titration solution consumed for titrating sample solution, expressed in mL;

M1--value of molar mass of sodium chloride, expressed in g/mol [M(NaCl)=58.4];

m4--mass value of sample, expressed in g.

Calculation result is rounded to 0.1.

A.4.2.5 Permissible difference

Absolute difference between two determination results is not more than 0.3 % (mass fraction) and arithmetic mean of the results is taken as determination result.

A.4.3 Determination of sulfate (based on Na2SO4)

A.4.3.1 Reagents and solutions

a) Sodium hydroxide solution: 0.2 g/L;

b) Hydrochloric acid solution: 1+1999;

c) Barium chloride standard titration solution: c(1/2BaCl2)=0.1 mol/L (see Annex C for

preparation method);

d) Phenolphthalein indicator solution: 10 g/L;

e) Rhodizonic acid disodium salt indicator solution: weigh 0.l g of rhodizonic acid disodium salt and dissolve in 10 mL of water (prepared freshly).

A.4.3.2 Determination procedures

Pipette 25 mL of sample solution (A.4.2.2 in this Standard) to a 250 mL conical flask, add 1 drop of phenolphthalein indicator solution, add sodium hydroxide solution dropwise to develop pink, then add hydrochloric acid solution dropwise until pink disappears, shake up, titrate with barium chloride standard titration solution while constantly shaking after dissolving, take rhodizonic acid disodium salt indicator solution as external titration solution, and considered that the reaction solution and the indicator solution develop rose red spots on the intersection of filter paper and last 2 min as end point.

Meanwhile, perform a blank test in the same way.

A.4.3.3 Result calculation

Sulfate (based on Na2SO4) is calculated according to formula (A.5) based on mass fraction w4 and its value is expressed in %:

$$w_4 = \frac{c_2[(V_2 - V_3)/1000](M_2/2)}{m_4(25/200)} \times 100 \quad \text{.....(A.5)}$$

where:

c2--accurate value of concentration of barium chloride standard titration solution, dropwise mol/L;

V2—accurate value of volume of barium chloride standard titration solution consumed for titrating sample solution, dropwise mL;

V3--accurate value of volume of barium chloride standard titration solution consumed for titrating blank solution, dropwise mL;

M2--value of molar mass of sodium sulfate, dropwise g/mol [M(Na2SO4)=142,04];

m4--mass value of sample, dropwise g.

Calculation result is rounded to 0.1.

A.4.3.4 Permissible difference

Absolute difference between two determination results is not more than 0.2% (mass fraction) and arithmetic mean of the results is taken as determination result.

A.4.4 Calculation results of total loss on drying, chloride (based on NaCl) and sulfate (based on Na2SO4)

Total of loss on drying, chloride (based on NaCl) and sulfate (based on Na2SO4) is calculated according to formula (A.6) based on mass fraction w5 and its value is expressed in %:

$$w_5 = w_2 + w_3 + w_4 \quad \text{.....(A.6)}$$

where:

w2--content of loss on drying, dropwise % (mass fraction);

w3--content of chloride (based on NaCl), dropwise % (mass fraction);

w4--content of sulfate (based on Na2SO4), dropwise % (mass fraction).

Calculation result is rounded to 0.1.

A.5 Determination of water insoluble matter

A.5.1 Apparatus

a) Sintered glass crucible: G4, and aperture: 5 μm - 15 μm;

b) Constant temperature oven.

A.5.2 Determination procedures

Weigh about 3 g of the sample (accurate to 0.001 g), place in a 500 mL beaker, add 250 mL of 50 - 60 ℃ hot water for dissolving, filter by a G4 sintered glass crucible baked to constant weight at 135 ◦C, fully wash until the cleaning solution is colorless, and bake in a 135℃ constant temperature oven to constant weight.

A.5.3 Result calculation

Water insoluble matter is calculated according to formula (A.7) based on mass fraction w6 and its value is expressed in %:

$$w_6 = \frac{m_6}{m_5} \times 100 \quad \text{.....} (A.7)$$

where:

m6--value of mass of dried water insoluble matter, expressed in g;

m5--mass value of sample, expressed in g.

Calculation result is rounded to 0.01.

A.5.4 Permissible difference

Absolute difference between two determination results is not more than 0.05 % (mass fraction) and arithmetic mean of the results is taken as determination result.

A.6 Determination of subsidiary colors

A.6.1 Method summary

Various components are separated and eluted by paper chromatography, and then quantified by spectrophotometry.

A.6.2 Reagents

a) Absolute ethyl alcohol;

b) N-butyl alcohol;

c) Acetone solution: 1+1;

d) Ammonia solution: 4+96;

e) Sodium bicarbonate solution: 4 g/L.

A.6.3 Apparatus and instruments

a) Spectrophotometer;

b) Chromatography filter paper: No. 1 medium-speed filter paper, 150 mm×250 mm;

c) Chromatography tank: φ240 mm×300 mm;

d) Micro sample injector: 100 μL;

e) Nessler tube: 50 mL, with ground glass stopper;

f) Sintered glass funnel: G3, aperture: 15 μm-40 μm;

g) 50 mm cuvette;

h) 10 mm cuvette.

A.6.4 Determination procedures

A.6.4.1 Conditions for paper chromatography

a) Developing solvent: n-butyl alcohol + absolute ethyl alcohol + ammonia solution = 6+2+3;

b) Temperature: 20 ◦C - 25 ◦C.

A.6.4.2 Preparation of sample solution

Weigh about 1 g of the sample (accurate to 0.001 g), place in a beaker, add a proper amount of water for dissolving, transfer to a 100 mL volumetric flask, dilute to volume and shake up for use. Concentration of the sample solution is 1 %.

A.6.4.3 Preparation of sample eluate

Absorb 100 μL of sample solution by a micro sample injector, evenly inject the sample solution on a baseline 25 mm from bottom edge of filter paper to form a straight line so that width of this sample solution on filter paper is not more than 5 mm and the length is 130 mm, and blow dry by an air blower. Place the filter paper in a chromatography tank with pre-prepared developing solvent for developing, and immerse the bottom edge of the filter paper 10 mm below the level of the developing solvent until the developing solvent rises to 150 mm along the line or subsidiary colors are separated to satisfaction. Take out chromatography filter paper and blow it dry with cold air.

Develop on blank filter paper under the same conditions. The blank filter paper must be taken from the adjacent part on the same filter paper as the filter paper used for developing in the above procedure.

See Fig. A.2 for schematic diagram of paper chromatography of subsidiary colors.

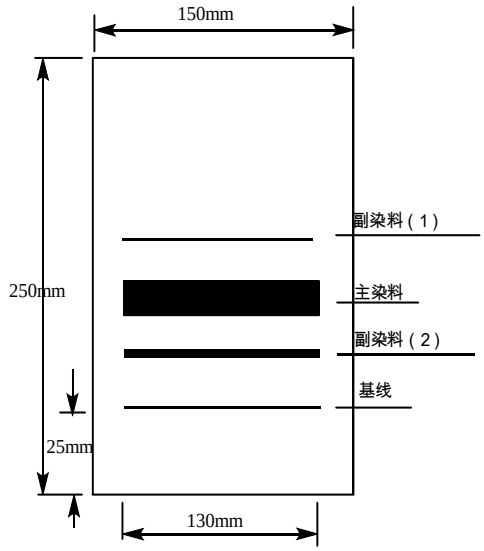


Fig A.2 Schematic diagram of paper chromatography of subsidiary colors

Cut various subsidiary colors obtained by developing and filter paper of the parts on blank filter paper corresponding to various subsidiary colors in the same size, cut into about 5 mm×15 mm thin strips, respectively place in 50 mL Nessler tubes, accurately add 5 mL of acetone solution, shake for 3 min - 5 min, then accurately add 20 mL of sodium bicarbonate solution, fully shake, and then respectively allow natural filtration in a sintered glass funnel, the filtrate must be clear without suspension. Add water to volume, and respectively obtain eluates of various subsidiary colors and blank solution. Measure absorbance values of sample eluates of various subsidiary

colors on the spectrophotometer by a 50 mm cuvette at the maximum absorption wavelength of various subsidiary colors.

When absorbance is determined on the spectrophotometer, mixture of 5 mL of acetone solution and 20 mL of sodium bicarbonate solution is taken as reference solution.

A.6.4.4 Preparation of standard solution

Absorb 2 mL of 1 % sample solution, transfer to a 100 mL volumetric flask, dilute to volume and shake up. This solution is standard solution.

A.6.4.5 Preparation of standard eluate

Absorb 100 μL of standard solution by a micro sample injector, evenly inject on a baseline 25 mm from bottom edge of filter paper, and blow it dry by an air blower. Place filter paper in a chromatography tank with pre-prepared developing solvent for developing, take out and blow it dry with cold air after developing solvent rises to 40 mm along the line, cut all developed color parts, and perform extraction operation according to the method in A.6.4.3 of this Standard to obtain standard eluates, measure absorbance values at the maximum absorption wavelength by a 10 mm cuvette.

Meanwhile, develop on blank filter paper under the same conditions and measure absorbance value of eluate after operation by the same method.

A.6.4.6 Result calculation

Subsidiary colors are calculated according to formula (A.8) based on mass fraction w7 and the value is expressed in %:

$$w_7 = \frac{[(A_1 - b_1) + \cdots\cdots + (A_n - b_n)]5}{(A_s - b_s)(100/2)} \times S \qquad (A.8)$$

where:

A1…, An--absorbance values of eluates of various subsidiary colors measured at 50 mm beam path distance;

b1…, bn--absorbance values of blank eluates of various subsidiary colors measured at 50 mm beam path distance;

As--absorbance value of standard eluate measured at 10 mm beam path distance;

bs--absorbance value of standard blank eluate measured at 10 mm beam path distance;

5--ratio converted into 10 mm beam path distance;

100/2--ratio of standard eluate converted into 1% sample solution;

S—content of sample, expressed in % (mass fraction).

Calculation result is rounded to 0.1.

A.6.4.7 Permissible difference

Absolute difference between two determination results is not more than 0.2 % (mass fraction) and arithmetic mean of the results is taken as determination result.

A.7 Determination of total of unreacted intermediates

A.7.1 Method summary

Use reverse liquid chromatography, quantify various unreacted intermediates by external standard method and finally calculate total of unreacted intermediates.

A.7.2 Reagents

a) Methanol;

b) Ammonium acetate solution: 2 g/L;

c) 1-acetamino-8-naphthol-3,6-disulfonic acid;

d) 1-amino-8-naphthol-3,6-disulfonic acid;

e) Sulfanilic acid.

A.7.3 Apparatus and instruments

a) Liquid chromatograph: infusion pump -- flow range: 0.1 mL/min - 5.0 mL/min, flow stability within this range: ± 1 %

Detector -- multi-wavelength UV spectrometric detector or UV spectrometric detector with same properties;

b) Chromatographic column: 150 mm long stainless column with inner diameter of 4.6 mm, fixed phase: C18, particle diameter: 5 μm;

c) Chromatographic work station or integrator;

d) Ultrasonic generator;

e) Injection loop: 20 μL.

A.7.4 Chromatographic conditions

a) Detection wavelength: 254 nm;

b) Column temperature: 40 ◦C;

c) Mobile phase: A: ammonium acetate solution; B: methanol;

Concentration gradient: 50 min linear concentration gradient from A:B (100:0) to A:B (0:100);

d) Flow: 1 mL/min;

e) Sample size: 20 μL.

The optimum analysis conditions can be selected for different apparatus and mobile phase is degassed by the ultrasonic generator after shaking up.

A.7.5 Preparation of sample solution

Weigh about 0.01 g of new red sample (accurate to 0.0001 g), add ammonium acetate solution and dilute to volume of 100 mL.

A.7.6 Preparation of standard solution

Weigh about 0.01 g (accurate to 0.0001 g), place in 1-acetamino-8-naphthol-3,6-disulfonic acid dried for 24 h in a vacuum drier, and dissolve in ammonium acetate solution and dilute to volume of 100 mL. Then, absorb 10 mL of this solution and dilute to volume of 100 mL by ammonium acetate solution, the resulting solution is taken as standard solution A.

Weigh about 0.01g (accurate to 0.0001 g), place in 1-amino-8-naphthol-3,6-disulfonic acid dried for 24 h in a vacuum drier, and dissolve in ammonium acetate solution and dilute to volume of 100 mL. Then, absorb 10 mL of this solution and dilute to volume of 100 mL by ammonium acetate solution, the resulting solution is taken as standard solution B.

Weigh about 0.01g (accurate to 0.0001 g), place in sulfanilic acid dried for 24 h in a vacuum drier, and dissolve in ammonium acetate solution and dilute to volume of 100 mL. Then, absorb 10 mL of this solution and dilute to volume of 100 mL by ammonium acetate solution, the resulting solution is taken as standard solution C.

Then, respectively absorb 10.0 mL, 5.0 mL, 2.0 mL and 1.0 mL of standard solution A, standard solution B and standard solution C, and dilute to volume of 100 mL by ammonium acetate solution respectively, and be prepare into A series standard solution, B series standard solution

and C series standard solution.

A.7.7 Determination procedures

Under chromatographic conditions specified in A.7.4 of this Standard, respectively absorb sample solution by micro sample injector and series standard solution and inject into injection loop for chromatographic detection, and process results after the last component is separated out. Determine peak area of standard solution matters of various series, and respectively draw standard curves A, B and C. Determine peak area of 1-acetamino-8-naphthol-3,6-disulfonic acid, 1-amino-8-naphthol-3,6-disulfonic acid and sulfanilic acid in sample solution, and calculate contents of various unreacted intermediates according to all standard curves (see Annex D for chromatogram).

A.7.8 Result calculation

Total of unreacted intermediates is calculated according to formula (A.9) based on mass fraction w11 and its value is expressed in %:

$$w_{11} = w_8 + w_9 + w_{10} \quad (A.9)$$

where:

--content of 1-acetamino-8-naphthol-3,6-disulfonic acid, expressed in % (mass fraction);

--content of 1-amino-8-naphthol-3,6-disulfonic acid, expressed in % (mass fraction);

--content of sulfanilic acid, expressed in % (mass fraction).

A.8 Determination of unsulfonated aromatic primary amine (based on aniline)

A.8.1 Method summary

The sample and aniline standard solution are compared after diazotization and coupling.

A.8.2 Reagents and solutions

a) Ethyl acetate;

b) Hydrochloric acid solution: 1+10;

c) Hydrochloric acid solution: 1+3;

d) Potassium bromide solution: 500 g/L;

e) Sodium carbonate solution: 200 g/L;

f) Sodium hydroxide solution: 40 g/L;

g) Sodium hydroxide solution: 4 g/L;

h) R salt solution: 20 g/L;

i) Sodium nitrite solution: 3.52 g/L;

j) Aniline standard solution: 0.1000 g/L;

Preparation: weigh about 0.5000 g of freshly distilled aniline by a small beaker, transfer to a 500 mL volumetric flask, wash the beaker for three times by 150 mL (1+3) hydrochloric acid solution respectively, incorporate the solution into 500 mL volumetric flask, and use water to dilute to volume. Transfer 25 mL of the resulting solution to a 250 mL volumetric flask and dilute to volume with water. Aniline concentration of the resulting solution is 0.1000 g/L.

A.8.3 Apparatus and instrument

a) Visible spectrophotometer;

b) 40 mm cuvette.

A.8.4 Preparation of sample extract solution

Weigh about 2.0 g of the sample (accurate to 0.001 g) to a 150 mL beaker, add 100 mL of water and 5 mL of (40 g/L) sodium hydroxide solution, and stir in lukewarm bath to complete dissolution. Transfer this solution to a separating funnel and wash the breaker clean by a small amount of water. Extract by 50 mL of ethyl acetate twice and combine extracts. Wash ethyl acetate extract by 10 mL (4 g/L) sodium hydroxide solution to remove trace colors. Then, perform three reverse extractions on ethyl acetate solution by 10 mL of (1+3) hydrochloric acid solution for three times. Combine hydrochloric acid extracts, then use water to dilute to 100 mL and shake up. The resulting solution is taken as sample extract solution.

A.8.5 Preparation of standard control solution

Absorb 2.0 mL of aniline standard solution to a 100 mL volumetric flask, dilute to volume with (1+10) hydrochloric acid solution and mix uniformly. This solution is standard control solution.

A.8.6 Preparation of diazo coupling solution

Respectively absorb 10 mL of sample extract solution and standard control solution, respectively transfer to transparent and clean test tubes, and immerse into a beaker with ice-water mixture for 10 min cooling. Respectively add 1 mL of potassium bromide solution and 0.5 mL of sodium nitrate solution to the test tubes, slightly shake up and still place in ice-water bath for 10 min cooling to perform diazo reaction. Respectively take another 25 mL volumetric flask and add 1 mL of R salt solution and 10 mL of sodium carbonate solution. Add aniline diazonium salt solution in the test tube to the volumetric flask with R salt solution, add while slightly shaking the volumetric flask, wash the test tube clean with a slight amount of water, add to the volumetric flask together, and then use water to dilute to volume. Mix fully and keep in a dark place for 15 min. The resulting solutions are respectively sample diazo coupling solution and standard diazo coupling solution.

A.8.7 Preparation of reference solution

Absorb 10 mL of (1+10) hydrochloric acid solution, 10 mL of sodium carbonate solution and 1 mL of R salt solution to a 25 mL volumetric flask, and dilute to volume with water. This solution is reference solution.

A.8.8 Determination procedures

Place standard diazo coupling solution and sample diazo coupling solution into cuvettes respectively, and measure respective absorbance Aa and Ab by spectrophotometer at 510 nm wavelength with the solution prepared in A.8.7 of this Standard as reference solution.

A.8.9 Result determination

If $Ab \leq Aa$, it is acceptable.

A.9 Determination of arsenic

A.9.1 Method summary

Digest new red with wet method and prepare into sample solution, and determine arsenic content by atomic absorption spectrometry.

A.9.2 Reagents and solutions

a) Nitric acid;

b) Sulfuric acid solution: 1+1;

c) Nitric acid-perchloric acid mixture: 3+1;

d) Arsenic (As) standard solution: prepare and calibrate according to GB/T 602, and then dilute and prepare into three standard solutions with corresponding arsenic concentration based

on requirements of apparatus used;

e) Sodium hydroxide solution: 1 g/L;

f) Sodium borohydride solution: 8 g/L (solvent is 1 g/L sodium hydroxide solution);

g) Hydrochloric acid solution: 1+10;

h) Potassium iodide solution: 200 g/L.

A.9.3 Apparatus

Atomic absorption spectrometer

Reference conditions of apparatus: analysis line wavelength of arsenic hollow cathode lamp: 193.7 nm; slit: 0.5 nm - 1.0 nm; lamp current: 6 mA - 10 mA;

Flow rate of carrier gas: 250 mL/min, argon gas;

Temperature of atomizer: 900 ◦C.

A.9.4 Determination procedures

A.9.4.1 Sample digestion

Weigh about 1.0 g of the sample (accurate to 0.001 g), place into a 250 mL conical flask or round bottom flask, add 10 mL - 15 mL of nitric acid and 2 mL of sulfuric acid, shake up, heat with low fire to remove nitrogen dioxide gas, stop heating when solution becomes brown, cool naturally and add 5 mL of nitric acid-perchloric acid mixture, heat with strong fire until the solution becomes transparent and colorless or yellowish, if the solution is still nontransparent, cool naturally and add 5 mL of nitric acid-perchloric acid mixture again, continue to heat until the solution becomes clear and colorless or yellowish and white smoke generates (carbonization shall be avoided due to burning out), stop heating, cool naturally and add 5 mL of water and heat to boil to remove residual nitric acid-perchloric acid (add water and boil again if necessary), continue to heat until white smoke generates, stand for 10 min, cool naturally and transfer to a 100 mL volumetric flask (filtration must be performed if the solution has turbidity, precipitate and mechanical impurities), and dilute to volume with hydrochloric acid solution.

Meanwhile, prepare blank solution by the same method.

A.9.4.2 Determination

Measure 25 mL of digested sample solution into a 50 mL volumetric flask, add 5 mL of potassium iodide solution, dilute to volume with hydrochloric acid solution, shake up and stand for 15 min.

Meanwhile, prepare blank test solution with blank solution by the same method.

Turn on apparatus, fully preheat apparatus and arsenic hollow cathode lamp, stabilize baseline, take sodium borohydride solution as a hydride reducing agent, and respectively inject standard blank solution, standard solution, sample blank test solution and sample solution in sequence according to computer instruction. After test, the computer automatically generates working curve and detect arsenic concentration of sample solution with sample blank solution deducted, and inputs sample information (name, sample weight, dilution volume, etc.), thus automatically calculating arsenic content of the sample.

A.9.5 Permissible difference

Absolute difference between two determination results is not more than 0.1 (mg/kg) and arithmetic mean of the results is taken as determination result.

A.10 Determination of lead

A.10.1 Method summary

Digest new red with wet method and prepare into sample solution, and determine content of lead by atomic absorption spectrometry.

A.10.2 Reagents and solutions

a) Lead (Pb) standard solution: prepare and calibrate according to GB/T 602, and then dilute and prepare into three standard solutions with corresponding lead concentration based on requirements of apparatus used;

b) Sodium hydroxide solution:1 g/L;

c) Sodium borohydride solution: 8 g/L (solvent is 1 g/L sodium hydroxide solution);

d) Hydrochloric acid solution: 1+10.

A.10.3 Apparatus

Atomic absorption spectrometer

Reference conditions of apparatus: Method 3 - Flame atomic absorption spectrometry in GB 5009.12.

A.10.4 Determination procedures

Sample solution and blank solution in A.9.4.1 of this Standard can be directly used.

Operate according to Method 3 - Flame atomic absorption spectrometry in GB 5009.12.

A.10.5 Permissible difference

Absolute difference between two determination results is not more than 1.0 (mg/kg) and arithmetic mean of the results is taken as determination result.

Annex B

(Normative)

Preparation Method of Titanium Trichloride Standard Titration Solution

B.1 Reagents and solutions

a) Hydrochloric acid;

b) Ammonium ferrous sulfate;

c) Ammonium thiocyanate solution: 200 g/L;

d) Sulfuric acid solution: 1+1;

e) Titanium trichloride solution;

f) Potassium dichromate standard titration solution: [c(1/6K2Cr2O7)=0.1 mol/L], and prepare and calibrate according to GB 602.

B.2 Apparatus

See Fig. A.1 in Annex A.

B.3 Preparation of titanium trichloride standard titration solution

B.3.1 Preparation

Take 100 mL of titanium trichloride solution and 75 mL of hydrochloric acid, place in a 1000 mL blown volumetric flask, dilute with water freshly boiled and then cooled to room temperature to volume, shake up, immediately pour into a bottle with bottom mouth away from light, and store under protection of carbon dioxide gas.

B.3.2 Calibration

Weigh about 3 g (accurate to 0.0001 g) of ammonium ferrous sulfate, place in a 500 mL conical

flask, add 50 mL freshly boiled and cooled water under protection carbon dioxide gas for dissolving, then add 25 mL of sulfuric acid solution, continue to introduce carbon dioxide gas under level for protection, rapidly and accurately add 35 mL of potassium dichromate standard titration solution, then titrate with titanium trichloride standard solution to be calibrated to approximate to the end point of calculated amount, immediately add 25 mL of ammonium thiocyanate solution, and continue to titrate with titanium trichloride standard solution to be calibrated until red changes into green at the end point. The whole titration process shall be operated under protection carbon dioxide gas, and perform a blank test at the same time.

B.3.3 Result calculation

Concentration of titanium trichloride standard solution is calculated according to formula (B.1) based on c(TiCl3), and its unit is mol/L:

$$c(TiCl_3) = \frac{cV_1}{V_2 - V_3} \quad \text{.....(B.1)}$$

where:

c--accurate value of concentration of potassium dichromate standard titration solution, expressed in mol/L;

V1--accurate value of volume of potassium dichromate standard titration solution, expressed in mL;

V2--accurate value of volume of titanium trichloride standard titration solution consumed for titrating high titanium oxidized by potassium dichromate standard titration solution, expressed in mL;

V3--accurate value of volume of titanium trichloride standard titration solution consumed for titrating blank solution, expressed in mL;

Calculation result is rounded to 0.0001.

The above calibration needs to be immediately performed during sample analysis.

Annex C

(Normative)

Preparation Method of Barium Chloride Standard Solution

C.1 Reagents and solutions

a) Barium chloride;

b) Ammonia water;

c) Sulfuric acid standard titration solution: [c(1/2H2SO4)=0.1 mol/L], and prepare and calibrate according to GB/T 601;

d) Rhodizonic acid disodium salt indicator solution (Weigh about 0.1 g of rhodizonic acid disodium salt and dissolve in 10 mL of water, and prepare the solution freshly);

e) Universal pH paper.

C.2 Preparation

Weigh about 12.25 g of barium chloride, dissolve in 500 mL of water, transfer to a 1000 mL volumetric flask, dilute to volume, and shake up.

C.3 Calibration method

Absorb 20 mL of sulfuric acid standard titration solution, place into a 250 mL conical flask, add 50 mL of water, neutralize with ammonia water to the universal pH paper indicates 8, then

titrate with barium chloride standard titration solution, take rhodizonic acid disodium salt indicator solution as external indicator solution, and consider that the reaction solution and the indicator solution develop rose red spots at the intersection of filter paper and last 2 min without fading as end point.

C.4 Result calculation

Concentration of barium chloride standard titration solution is calculated according to formula (C.1) based on c(1/2BaCl2), and its unit is mol/L:

$$c(\frac{1}{2}BaCl_2)=\frac{c_1V_4}{V_5}\text{.....}(C.1)$$

where:

c1--accurate value of concentration of sulfuric acid standard titration solution, expressed in mol/L;

V4--accurate value of volume of sulfuric acid standard titration solution, expressed in mL;

V5--accurate value of volume of barium chloride standard titration solution used, expressed in mL.

Calculation result is rounded to 0.0001.

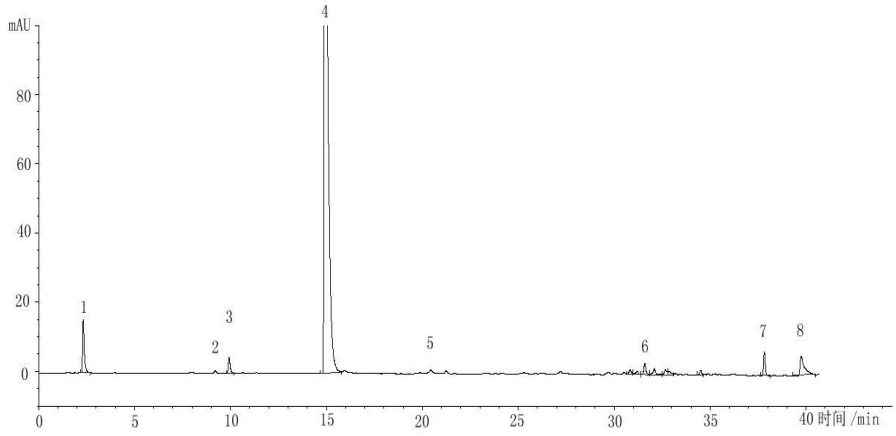
Annex D

(Normative)

Liquid Chromatogram of New Red and retention time of Components

D.1 Liquid chromatogram of new red

See Fig. D.1 for liquid chromatogram of new red.



1. 1-amino-8-naphthol-3,6-disulfonic acid;
2. 1-acetamino-8-naphthol-3,6-disulfonic acid;
3. Sodium sulfanilate;
4. New red;
5. Unknown matter;
6. Unknown matter;
7. Unknown matter;

8. Unknown matter.

Fig. D.1 Liquid chromatogram of new red

D.2 Retention time of components of new red

See Table D.1 for retention time of components of new red

Table D.1 Retention time of components of new red

Peak No.	Name of component	Retention time (min)
1	1-amino-8-naphthol-3,6-disulfonic acid	2:19
2	1-acetamino-8-naphthol-3,6-disulfonic acid	9:20
3	Sodium sulfanilate	9:95
4	New red	15:32

Peak No. Name of component Retention time (min)

1 1-amino-8-naphthol-3,6-disulfonic acid 2:19

2 1-acetamino-8-naphthol-3,6-disulfonic acid 9:20

3 Sodium sulfanilate 9:95

4 New red 15:32

Note: Retention time of components of samples may vary in accordance with apparatuses, separating columns, and even in accordance with injection time, but the elution order of various components is the same.

END TRANSLATION